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Oxygen Problem - Report XII
Report to M.R.R.C. No. 8

MONTHLY REPORT

February 14, 1942 to March 14, 1942

CONTRACT NUMBER ONKsr-213

DEVELOPMENT OF OXYGEN-CARRIERS

9-8 3-14-42
Driehl-
Report
11-225
102.211

This report summarizes the work done on this project since the submission of the monthly report of February 14, 1942 and summarizes material to be found in more detailed reports Nos. 4, 5, 6, 7 and 8 and in detailed reports in preparation.

A study was made of the oxygen-carrying capacity of diisocylalethylenediamine cobalt in chloroform solution. The experiment was run at constant temperature, the removal of oxygen being attempted by sweeping with carbon dioxide. No oxygen enrichment of the gases isolated was found.

Further studies were made on the preparation of diisocylalpropylenediamine cobalt; various modifications of the method of preparation, including the pyridine method were tried. None of the preparations made carried oxygen. Propylenediamine was resolved by fractional crystallization of its bitartrate, and the active propylenediamines so prepared were condensed with salicylaldehyde. The condensation product could not be induced to crystallize, and yielded cobalt compounds which were not active as oxygen-carriers.

Further consideration was given to the proposal to prove the existence of water in the parent oxygen-carrying compound by the use of radio-active water. It was decided that the difficulties were too great and the results too uncertain to warrant the necessary expenditure of time.

Some further study was made of the substitution of other diamines for ethylenediamine in the parent oxygen-carrying compound, but no active compounds were discovered.

Construction was continued on the differential, manometric apparatus designed to permit the measurement of oxygen absorption at various temperatures and pressures. The construction has been completed and the apparatus is ready for use except for the elimination of leaks. A suitable refrigerator for this work has been obtained.

The work on the methyl substituted salicylaldehydes was continued. The aldehyde derived from p-cresol gave, after



condensation with ethylenediamine, a cobalt compound which carried 3.0 per cent oxygen but was apparently less rapid in its absorption of oxygen on exposure to air than the parent compound. Of the two aldehydes derived from m-cresol, one gave a cobalt compound which was inactive, and the other a cobalt compound which carried 2.5 per cent oxygen but was apparently less rapid than the parent compound. The aldehyde derived from o-cresol gave a cobalt compound which was inactive. The synthesis of these methyl substituted salicylaldehydes was carried out by the Reimer-Tiemann reaction which gives exceptionally poor yields, and the work has therefore been quite time consuming. This work cannot be considered as having been completed as yet.

Attempts were made to improve the yield of the Reimer-Tiemann reaction by the introduction into the reaction mixture of cobalt salts and of ethylenediamine in the synthesis of salicylaldehyde from phenol. No improvement in the yield was found.

It was found that 3-methoxysalicylaldehyde and ethylenediamine yielded an active cobalt compound which carried practically the theoretical amount of oxygen (4.13 per cent) after having been heated to 170°. A satisfactory method of synthesis of this compound has now been devised. Although no precise rate studies have been made on the material, preliminary experiments indicate that the material absorbs oxygen more rapidly than the parent compound on exposure to air.

Considerable attention was devoted to the nitration of salicylaldehyde. The nitration was attempted by the action of nitrogen dioxide on solid cobalt salicylaldehyde, on cobalt salicylaldehyde suspended in carbon tetrachloride, and on solid disalicylaethylenediamine cobalt; the results were unsatisfactory. Attention was then returned to the direct nitration of salicylaldehyde in acetic acid with nitric acid. This nitration is not particularly difficult but yields a mixture of about equal amounts of 3-nitrosalicylaldehyde and 5-nitrosalicylaldehyde with a combined yield of about 80 per cent.

The separation of the two isomers can be easily accomplished by the fractional crystallization of the sodium salts. 3-Nitrosalicylaldehyde itself, however, is difficult to purify, becoming readily contaminated on short standing, after having been obtained pure, by a low melting material which is apparently a second crystal modification of the material. A satisfactory method of obtaining 3-nitrosalicylaldehyde in pure, high-melting form was devised. Three different condensation products of 3-nitrosalicylaldehyde with ethylenediamine were found. From these an oxygen-carrying, cobalt derivative was obtained which carried 3.83 per cent oxygen, which is the theoretical value

for one oxygen atom per one cobalt atom. The oxygen absorption of this compound on exposure to air is considerably faster than the oxygen absorption of the parent compound on exposure to air. However, first formal rate studies with pure oxygen indicate that the behavior of this material departs from that of the parent compound, and that although initially it absorbs oxygen much more rapidly, its over-all rate of oxygen absorption may not be any faster than the parent compound. The compound is destroyed at temperatures above 150°. The material is quite hygroscopic, but can be very readily converted from the non-active, hydrated material back to an active, anhydrous material. The low melting form of 3-nitrosalicylaldehyde was not obtained in pure form. It is provisionally assumed to be a hydrogen-bonding isomer (perhaps the first known) of the high-melting form. Preparation of the cobalt compound from material containing an appreciable amount of the low melting form were found to have a much lower oxygen-carrying capacity.

5-Nitrosalicylaldehyde did not yield an oxygen-carrying compound with ethylenediamine and cobalt.

Salicylaldehyde was brominated and the 5-bromo salicylaldehyde produced was condensed with ethylenediamine. A cobalt derivative of this material was prepared in a variety of different ways, all of which yielded inactive material.

The reaction between anhydrous cobalt salts and disalicyl-ethylenediamine was carried out under anhydrous conditions and two products were found, a green crystalline material, and an orange crystalline material, both of which did not carry oxygen. On treatment with water, these materials yielded oxygen-carrying compounds; the green material, gave a compound carrying 3.3 per cent oxygen, and the orange material gave a compound carrying 4.6 per cent oxygen. The orange material is undoubtedly the same as the orange material first precipitated in the Harrison-Mach method of producing the parent compound. The oxygen-carrying compound derived from the green material is probably the same material as that obtained by Tsuraki, being a compound which absorbs one-third of a molecule of oxygen per cobalt atom. The significance of this work lies in the bearing it has on the presence of a bridging group in the active oxygen-carrying compound.

Resacetophenone was synthesized, condensed with ethylenediamine, and a cobalt derivative of the condensation product prepared. The cobalt derivative was found to be weakly active as an oxygen-carrier.

During the month the Official Investigator visited the Latimer-Calvin group at the University of California. The experiences of both groups relative the synthesis of oxygen-carrying compounds, and the design of apparatus for testing

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oxygen-carrying compounds and for the manufacture of oxygen using these compounds were discussed. Steps were taken to integrate the research programs of the two groups in order that further duplication of efforts be avoided.

The results of the work carried out on this contract from December 1, 1941 to date will be made a subject of an extended report within the next month.

Ames, Iowa
March 14, 1942

Harvey Diehl
Official Investigator

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ABSTRACT:

Monthly progress report is given which summarizes the work done on development of oxygen-carriers. A study was made of the oxygen-carrying capacity of disalicylalethylene-dilmine cobalt in chloroform solution. Further studies were made on the preparation of disalicylalpropylenediimine; various modifications of the preparation, including the pyridine method, were tried. Further consideration was given to the proposal to prove the existence of water in the parent oxygen-carrying compound by the use of radioactive water. Construction was continued on the differential manometric apparatus designed to permit the measurement of oxygen absorption at various temperatures and pressures. Attempts were made to improve the yield of the Reimer-Tiemann reaction. Considerable attention was devoted to the nitration of salicylaldehyde. The reaction between anhydrous cobalt salts and disalicylalethylenediimine was carried out under anhydrous conditions.

DISTRIBUTION: Copies of this report obtainable from Air Documents Division; Attn: MCIDXD

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